10 618 556
01-08-04

(12) UK Patent Application (19) GB (11) 2 170 206 A

(43) Application published 30 Jul 1986

(21) Application No 8509939

(22) Date of filing 18 Apr 1985

(30) Priority data
(31) 3502993 (32) 30 Jan 1985 (33) DE

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(51) INT CL[4]
C08J 3/22

(52) Domestic classification (Edition H):
C3L EJ
C3W 111 113 208 217
U1S 1420 1573 2055 2318 C3L

(56) Documents cited
None

(58) Field of search
C3L
C3J
Selected US specifications from IPC sub-class C08J

(54) Preparing extrudable compositions

(57) To prepare extrudable compounds which, after the grafting on of silanes, are crosslinkable through the action of moisture, the filler and/or the pigment and/or the carbon black are added in the form of a highly concentrated free-flowing mixture (masterbatch) to the base mixture chronologically after the free-flowing particles of the base materials have been wetted with at least the silane component.

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SPECIFICATION

Preparing extrudable compositions

This invention relates to a process for preparing an extrudable composition incorporating one or more pigments and/or carbon black and/or one or more other colouring, stabilising or filling constituents, in addition to a base material comprising a thermoplastic or elastomeric material or a thermoplastic rubber, the base material being crosslinkable by the action of moisture and in the presence of a catalyst following the grafting of silane molecules on to the base material molecules by means of a peroxide, and the silane being added in liquid form with or without one or more further additives (in liquid form or in the form of a solution in the silane) to the base material in free-flowing pulverulent-to-granular form in a compounding operation performed with material temperatures equal to or not significantly exceeding room temperature.

To prepare plastics products of elevated heat-distortion resistance and ageing resistance, it is already known to crosslink polymeric materials by a form of crosslinking which has become established in the art under the name of the siloxane technique. In this technique, in contrast to customary peroxidic crosslinking, the macromolecules of the base polymer have grafted on to them low molecular weight compounds which (in the course of secondary reactions) permit the crosslinking of the macromolecules. It has been found to be particularly suitable to use, e.g. in grafting on to polyethylene molecules, certain polyfunctional organosilanes which possess an unsaturated vinyl group and readily hydrolysable alkoxy groups. In the grafted state, the polyethylene is still thermoplastic. The crosslinking of the material is the result of the conversion, as a first step under the influence of minute amounts of moisture, of the alkoxy groups on the silicon atoms into silanol groups. These then participate in condensation reactions to form siloxane crosslinking bridges between the individual macromolecules. This crosslinking technique permits particularly efficient production of crosslinkable products.

However, problems arise when materials which are thus crosslinkable are to be filled with inorganic fillers, as is commonly desirable in materials submitted to peroxidic crosslinking, e.g. to save polymeric material, or to confer on the product particular properties, for example UV resistance (conferred by compounding with carbon black) or a specific coloration (obtained by addition of pigment). These problems can arise because moisture bonded adsorpively to the filler can easily cause crosslinking to take place prematurely, during the grafting process itself. The consequences are a poor, inhomogeneous quality of melt and an unattractive extrudate surface.

To overcome these problems, German Laid-Open Specification (Offenlegungschrift) 2,856,381 proposes premixing the polymer (a homopolymer or copolymer of ethylene) with the fillers under dry conditions, homogenising, granulating, subsequently diffusing the silane compounds at room temperature or a little above into the material thus prepared or already present in this prepared form, blending this granulate containing the crosslinking agents with a polymer batch containing the antioxidants and the cross-linking catalyst, and finally grafting this granulate in an extrusion process and shaping it in the same operation. A process of this type permits the production of products having satisfactory surface properties, and can avoid premature crosslinking.

It has been found, however, that the polymer material which is first blended and granulated with the filler and then wetted with the silane compounds has only a comparatively short shelf life in that state, and thus as a rule requires early consumption. That constitutes a considerable restriction, however, particularly for the manufacturers and distributors of the compositions.

It is an object of the present invention, therefore, to enable the shelf life of the initially described compositions to be increased without obliging processors to accept lower levels of quality and difficulties in subsequent processing.

According to the present invention, there is provided a process for preparing an extrudable composition incorporating one or more pigments and/or carbon black and/or one or more other colouring, stabilising or filling constituents, in addition to a base material comprising a thermoplastic or elastomeric material or a thermoplastic rubber, the base material being crosslinkable by the action of moisture and in the presence of a catalyst following the grafting of silane molecules on to the base material molecules by means of a peroxide, and the silane being added in liquid form with or without one or more further additives (in liquid form or in the form of a solution in the silane) to the base material in free-flowing pulverulant-to-granular form in a compounding operation performed with material temperatures equal to or not significantly exceeding room temperature, wherein, at a stage subsequent to the wetting of the free-flowing particles of the base material with at least the silane component, the pigment(s) and/or carbon black and/or other colouring, stabilising or filling material(s) are added in the form of at least one free-flowing masterbatch.

As will be appreciated from the foregoing statement, filling materials, for example a carbon black, are not to be in homogeneous dispersion in the base material at the time at which the silane component is added. Instead, the silane component is added first, and distributed throughout the base material; as time goes on, the silane component is able to diffuse into the base

material. The stage of distribution and diffusion is followed by the incorporation of the masterbatch just specified. Compositions prepared by this process have shelf lives of months during which the quality remains constant.

After the diffusion of the silane component it is possible to incorporate carbon blacks, coloured pigments, or chalks, for example, directly or as concentrates at different times. In a particularly advantageous procedure, the masterbatch specified (for example of a light-coloured filler) is added to the silane-wetted base material, which can be for example a polyethylene granulate, after the base material has been silane wetted, but still as part of the same compounding operation. This "one-step" compounding technique which typically comprises a cold-compounding procedure, is a very economical and inexpensive form of processing for the compounder.

In another advantageous procedure, the masterbatch specified is brought together with the silane-wetted base material in the intake funnel of a grafted material forming extruder. As a result of the substantial diffusion of the silane component into the base material after a certain storage time, only base material particles which are already superficially substantially free of silane residues are brought into contact with the filler component. However, in the case of this method, separate storage is called for.

In a further usefule procedure, the masterbatch specified is added to the silane-wetted base material in a separate second cold-compounding operation after diffusion of some of the silane into the base material.

The adoption of these procedures will depend largely on what machinery is available to the compounder and on the amount of material contained in a batch.

If preference is given to the "one-step" procedure wherein the masterbatch is added to the base material at the end of the silane wetting phase, the compounding of the base material and silane component advantageously takes 1 to 8 min, preferably 2 to 5 min, at temperatures of 18°C to 40°C. The bulk of the silane used for the crosslinking is then already homogeneously distributed through the base material, and the small remainder which is absorbed by the masterbatch introduced is not sufficient to have an adverse effect on the shelf life, or even to promote incipient crosslinking during grafting and moulding of the composition in an extrusion stage.

The nature and amount of the additives which are added by means of the present masterbatch ultimately depend on the intended use for the specific composition concerned. For instance, in "facade" cables for outdoor suspension, a compound which is filled with carbon black will be used, inter alia also to obtain protection against UV radiation. In this context, it has been found to be advantageous to use a highly textured non-hygroscopic carbon black. The carbon black can have a BET surface area of 50–120 m^2/g. The amount of the carbon black masterbatch is advantageously chosen to be, for example, of the order of magnitude from 4 to 40, preferably 6 to 15, parts per 100 parts of base material, the carbon black masterbatch being assumed to have a carbon black content of about 40%.

In the case of underground cables it is a common practice to arrange for the insulation to be coloured. For this purpose it has been found to be suitable when carrying out the process of the invention to add to the base material a colouring agent masterbatch in an amount of 0.1 to 5, e.g. 0.3 to 2, parts per 100 parts of base material.

The invention will now be explained in more detail in the following Examples.

Examples 1 & 2

These employ the following formulations:

Example 1

polyethylene	100 parts
stabiliser masterbatch	5 parts
silane	1.5 parts
peroxide	0.04–0.08 part
catalyst	0.06 part
carbon black masterbatch	6.5 parts

Example 2

polyethylene	100 parts
stabiliser masterbatch	- parts
silane	1.5 parts
peroxide	0.04–0.08 part
catalyst	0.06 part
carbon black masterbatch	6.5 parts

To prepare a composition which is crosslinkable by moisture and is suitable for use for

insulating low-voltage facade cables, the procedure is for example that the polyethylene granulate having a melt flow index of for example 0.3, if desired together with a stabiliser masterbatch (see Example 1), is wetted at temperatures far below the crystallite melting point, i.e. as a rule at about room temperature, with the liquid component comprising the silane, the peroxide and if desired the catalyst as well as any other additives, such as antioxidants and so on, in a slow-speed mixer. After about 2 to 3 min the carbon black masterbatch is added to this mixture in granular form and is mechanically distributed in the base material as part of the same compounding operation. The compound thus prepared is packaged and is stored in the sealed packing until consumption, which can be intended in 2 or 3 months.

The nonhygroscopic carbon black used is advantageously an acetylene black. Acetylene blacks are known for example under the tradenames Shawinigan-Russ, Akzo-Russm Ketjen black EC and Azetylenschwarz y 200.

The peroxide used can be the peroxide which is at present the most common, namely a dicumyl peroxide, but peroxide blends, such as 1,3-bis (tert.-butylperoxisopropyl) benzene in combination with tert.-butyl peroxyisononanate, are suitable for carrying out the process of the invention.

Example 3

copolymer of polyethylene	100parts
vinyltrimethoxysilane	1.6parts
peroxide	0.05part
catalyst	0.05part
carbon black masterbatch	6.2parts

This compound can for example also be used for sheathing pipes or pipe-lines. To prepare the crosslinkable compound, the base material can be coated with the liquid silane-containing component, and the carbon black masterbatch then brought together at the intake funnel of the graft extruder of a process installation, for example by means of a so-called colorimeter, with the silanated (coated) base mixture, and in the course of the melting the carbon black is homogeneously distributed in the mixture.

Example 4

polyethylene	65parts
ethylene-propylene rubber	35parts
silane	2.0parts
peroxide	0.04part
antioxidant	0.35part
crosslinking catalyst	0.05part
coloured pigment masterbatch	0.8part

This compound which may for example have a red colour can be advantageously used as a sheath compound for underground cables. The preparation of the moisture-crosslinkable compound can be effected as in the previous Examples or by adding the pigment masterbatch in a separate cold-compounding process after the base material has been coated with the liquid silane component.

CLAIMS

1. Process for preparing an extrudable composition incorporating one or more pigments and/or carbon black and/or one or more other colouring, stabilising or filling constituents, in addition to a base material comprising a thermoplastic or elastomeric material or a thermoplastic rubber, the base material being crosslinkable by the action of moisture and in the presence of a catalyst following the grafting of silane molecules on to the base material molecules by means of a peroxide, and the silane being added in liquid form with or without one or more further additives (in liquid form or in the form of a solution in the silane) to the base material in free-flowing pulverulent-to-granular form in a compounding operation performed with material temperatures equal to or not significantly exceeding room temperature, wherein, at a stage subsequent to the wetting of the free-flowing particles of the base material with at least the silane component, the pigment(s) and/or carbon black and/or other colouring, stabilising or filling material(s) are added in the form of at least one free-flowing masterbatch.

2. Process according to claim 1, wherein the masterbatch specified is added to the silane-wetted base material only at the end of the silane wetting phase but still within the same compounding operation.

3. Process according to claim 1, wherein the masterbatch specified is brought together with the silane-wetted base material in the intake funnel of a grafted material forming extruder.

4. Process according to claim 1, wherein the masterbatch specified is added to the silane-

wetted base material in a separate second cold-compounding operation after some of the silane has diffused into the base material.

5. Process according to claim 2, wherein the compounding of the base material and silane takes 1 to 8 min, preferably 2 to 5 min, at temperatures of 18° to 40°C.

6. Process according to any of claims 1 to 5, wherein the masterbatch specified contains a highly textured non-hygroscopic carbon black.

7. Process according to claim 6, wherein, through the addition of the masterbatch specified, the final composition contains 1.5 to 15% of carbon black, preferably 2 to 5% of carbon black.

8. Process according to any of claims 1 to 7, wherein one or more pigments or other colouring agents are added in the form of a masterbatch to the silane-wetted base material in an amount of 0.1 to 5 parts, relative to the base material.

9. Process according to any of claims 1 to 8, wherein, through the addition of a masterbatch which contains a low-hygroscopicity filler, the final composition contains 5 to 40% by weight, preferably 10 to 20% by weight, of filler.

10. Process according to claim 1, substantially as described in any of the foregoing Examples.

11. An extrudable composition prepared by a process according to any of claims 1 to 10.

12. A cable, pipe or other elongate material having a sheath derived from a composition as claimed in claim 11 extruded around it.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.